Energetically favorable sites of iodine atoms in zirconium crystal : an ab-initio approach

G. Carlot, D. Davesne

LYCEN 2001-17

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G. Carlot and D. Davesne
carlot@ipnl.in2p3.fr and davesne@ipnl.in2p3.fr

March 28, 2001

IPN Lyon, 43 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex

Abstract

This paper is devoted to the determination of the energetically favorable sites of iodine atoms in zirconium crystal within the density functional framework and using norm-conserving pseudopotentials. We show that the substitutional sites are preferentially occupied compared to the interstitial ones. Our conclusion is that the diffusion process of iodine inside zirconium is of substitutional type in perfect agreement with an experimental study [Carlot 2000].

1 Introduction

Zirconium is a constitutive element of a great number of very important alloys like Zircaloy-4 in the context of nuclear industry (cladding tubes). In one hand Zircaloy-4 contains actually mainly Zr and only a small amount of Sn, Fe and Cr (less than 1% atomic) and in the other hand ab initio total energy calculations with several elements are known to be quite an impossible task. Therefore it makes sense to consider pure Zr metal to do some numerical simulations on that alloy.

In the nuclear fuel cycle, Zircaloy-4 (therefore zirconium) is the first barrier for fission products. Amongst them ^{129}I is probably one of the most problematic because of its volatile character and its very long period ($T = 1.59 \times 10^7$ years). Therefore, one has to be sure that the diffusion of

iodine inside zirconium is very small. However, it turns out that computing a diffusion coefficient from molecular dynamics is quite difficult : because of its smallness ($D \approx 10^{-23}$ cm^2.s^{-1} at 600°C [Carlot 2000]) the computational time would be too important (say several years even with the most efficient computers and algorithms). Nevertheless, what we can do is to obtain some indirect informations on the diffusion process itself (diffusion by substitutional or by interstitial mechanisms) by the determination of the preferential occupied sites (substitutional or interstitial). Effectively an element in a substitutional site (respectively interstitial) will diffuse by a substitutional (respectively interstitial) mechanism. Lots of diffusion studies have been realized in zirconium. Hood [Hood 1988] has done a synthesis of these studies and defined field of substitutional diffusion coefficient values. So if substitutional site is energetically favorable, we could have an idea on the value of the diffusion coefficient and the value of the activation energy of the diffusion of iodine in zirconium.
Therefore, we will concentrate in this paper on the determination of the energetically favorable sites of iodine atoms in zirconium crystal. The method used is based on density functional (Born and Oppenheimer 1927; Khon and Sham 1965; Hohenberg and Khon 1964) and pseudopotential theories (Hamann, Schlüter and Chiang 1979; Troullier and Martins 1991). The first part will be devoted to the description and the validation of the pseudopotentials of zirconium and iodine elements. Then, in the second part we will focus on the main result of this paper, that is, the location of iodine atoms in zirconium.

2 Construction and validation of pseudopotentials

2.1 Zirconium

The norm-conserving pseudopotential of Troullier-Martins (Troullier and Martins 1991) type used in this work has been generated for the zirconium with the FHI98PP code [Fuchs and Scheffler 1999]. We have started from a mixed configuration : the fundamental one ([Kr]4d^{2}5s^2) and a ionized one ([Kr]4d^{2}5s$^{0.8}$5p$^{0.2}$). Moreover, only the four external electrons have been treated as valence electrons. The cutoff radii for s, p and d angular momentum are respectively 2.91, 3.06 and 2.58 Bohr. The s component has

been chosen as the local potential and a Kleinman-Bylander (Kleinman and Bylander 80) form has been used. Finally, we have examined four approximations for the exchange-correlation potential : the local density approximation (LDA), the generalized-gradient approximation (GGA), and both with a core density cutoff radius. In the case of LDA calculations, we have considered the Ceperley-Alder [Ceperley and Alder 1980] parameterization and in the GGA case the one from Perdew and Wang [Perdew and Wang 1992].

In order to validate this pseudopotential, we now turn our attention to the construction of zirconium crystal. We recall below several important experimental data (Swanson 1953; Xia, Duclos, Ruoff and Vohra 1990; Xia and Parthasarathy 1990; Jayaraman, Klement and Kennedy1963; Pascal IX) and present the conventions used in this work.

At room temperature, zirconium exhibits an interesting crystal structure sequence :

$$\alpha - Zr \overset{2-6GPa}{\rightarrow} \omega - Zr \overset{30GPa}{\rightarrow} \beta - Zr$$

The α phase displays a closed hexagonal structure with c/a ratio equal to 1.593 ($a = 3.23\mathring{A}$ and $c = 5.15\mathring{A}$). This structure has two atoms per unit cell. Following Wyckoff conventions, the atomic positions are $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ and $(\frac{2}{3},\frac{1}{3},\frac{3}{4})$. The space group is $P6_3/mmc$. The ω phase displays a simple hexagonal structure with c/a ratio equals to 0.625 and with three atoms per unit cell. The atomic positions are (0,0,0), $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$ and the space group is P6/mmm. Finally the β phase displays a centered cubic structure ($a = 3.54\mathring{A}$) with one atom per unit cell located at (0,0,0). Its space group is Im3m.

We have now to reproduce some physical quantities. To reach this goal, we plot, for each of the three phases, the energy per atom with respect to the volume. These curves allow us to extract the equilibrium volume V_0 (and consequently the cell parameter a), the bulk modulus B_0 and its first derivative B_0' via an empirical fit (see Murnaghan [Murnaghan 1944]) :

$$E(V) = E(V_0) + \frac{B_0 V}{B_0'(B_0'-1)}\left[B_0'\left(1-\frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \qquad (1)$$

In order to have an accurate estimate of these parameters, the number of k-points in the irreducible Brillouin zone (that determines the number of plane waves) and the cut-off energy E_C (that determines the largest value of k) must be adjusted. Effectively, there is a compromise between a high

accuracy of the result (that involves in general a great number of k-points and a very large value for E_c) and the required time to obtain this accurate result. In practice, we have fixed the number of k-points to a very large value and looked at the variations of the parameters with increasing E_c. Results are presented in Figure 1. Then, for the value of E_c the convergence was obtained, we looked at the variations of the parameters with respect to the number of k-points (see Figure 2). Note also that we have chosen the k-points according to Monkhorst [Monkhorst 1976].

The final result is the following : to obtain results available up to 0.01 eV, we have to use a 18×18×9 k-points mesh for the α phase, a 8×8×16 mesh for the ω phase, and a 12×12×12 mesh for the β case. Concerning E_C, we fixed it at 30 Ry for the three phases. The corresponding curves for the total energy with respect to the volume are presented in Figure 3 for each phase and for the four exchange-correlation energy approximation schemes. Three of these schemes (GGA,GGA with 2.0 Bohr and LDA with 2.0 Bohr) exhibit the correct crystallographic sequence $\alpha \rightarrow \omega \rightarrow \beta$ with decreasing volume. The values for equilibrium volumes and bulk modulus are presented in Tables 1 and 2. The comparison between our values and experimental data (Swanson 1953; Xia, Duclos, Ruoff and Vohra 1990; Xia and Parthasarathy 1990; Jayaraman and Klement 1963; Pascal IX) or other values obtained by calculations in the literature (Jomard, Magaud and Pasturel 1998) clearly indicates that the GGA pseudopotential generated with a core density cutoff radius equals to 2.0 Bohr gives the best results. Also deduced from the same curves and presented in Table 3 is the transition pressure between α phase and ω phase. For that parameter again the best agreement is obtained for GGA with 2.0 Bohr. However, we should mention that in our study, it is impossible to determine the transition pressure between ω phase and β phase. This is a real problem if one wants to have an "absolute" pseudopotential for the zirconium. But actually, what we want to do here is to incorporate iodine atoms in a crystal of zirconium (α-phase) and let the entire crystal relaxed. So, we have to be sure that during this period, the crystal does not relax to an other crystallographic phase. Since, the α-phase is the most stable phase (see Figure 3), so it does not matter if the β-phase is less stable than it should be. In any case, this problem would disappear if one uses a pseudopotential with 10 valence electrons [Jomard, Magaud and Pasturel 1998]. In conclusion, this problem of relative stability is not important from a physical point of view for our aim and our pseudopotential is much less time-consuming because it has only four valence electrons. So we will use it in the following.

2.2 Iodine

For the iodine ([Kr]$4d^{10}5s^25p^5$) pseudopotential, we have used the same method. Its main features are : seven valence electrons ($5s^25p^5$), local s component and LDA/GGA approximations for the exchange-correlation energy with and without a core density cutoff radius equals to 2.0 Bohr.

For the validation of this pseudopotential, we have worked on the molecular iodine I_2 and tried to reproduce the following relevant physical quantities : the vibration frequency (with a molecular dynamics simulation), the equilibrium bond distance (by a relaxation run) and the dissociation energy. The first step was, as before, to adjust the number of k-points and the cutoff energy. We worked with a $10\times10\times10$ k-points mesh and E_C=30 Ry to obtain the same accuracy. The results are presented in the Table 4. We can see that our calculations are in good agreement with the experimental data [Pascal XVI, Handbook 74^{TH}]. Our "best" pseudopotential is, as in the preceding section, the GGA one with a density cutoff radius.

We are now in position of including iodine atoms in zirconium crystal (α phase) in order to determine the preferential site for iodine. To access this result, we have to build cells of various types. These cells will contain either N zirconium atoms or $N-1$ zirconium atoms and one vacancy or $N-1$ zirconium atoms and one iodine atom in substitutional position or N zirconium atoms and one iodine atom in interstitial position. For each of these cases, we will do a total energy minimization run. This will give us the vacancy formation energy, the impurity energy and the incorporation energy. These energies calculations have been realized with FHI98MD (Kley, Neugebauer and Scheffler 1997) code. As recalled below these energies give us informations on the preferential site for iodine.

3 Calculation of the vacancy zirconium formation energy and incorporation and impurity energies of iodine in zirconium

3.1 Definitions.

- The vacancy formation energy is defined by [Braun, Fähnle, Schilfgaarde and Jepsen 1995, Korhonen, Puska and Nieminen 1995] :

$$E_{f_{vacancy}} = E_{Zr_{(N-1),vacancy}} - \left(\frac{N-1}{N}\right) E_{Zr_N}$$

where $E_{Zr_{(N-1),vacancy}}$ is the total energy of the cell which contains $N-1$ atoms of zirconium and one vacancy and E_{Zr_N} is the total energy of the perfect cell which contains N atoms of zirconium. It represents the energy required to move an atom from the crystal to infinity.

- The impurity energy is the energy necessary to substitute a zirconium atom by a iodine atom in the crystal [Grimes, Catlow and Stoneham 1989, Grimes and Catlow 1991]. It is determined by the relation :

$$E_{impurity} = E_{(Zr_{(N-1)},I)} + E_{Zr} - E_{Zr_N} - E_I$$

where $E_{(Zr_{(N-1)},I)}$ is the total energy of the cell with $N-1$ atoms of zirconium and iodine atom in substitution and $E_I(E_{Zr})$ is the energy of the atom of iodine (zirconium) alone. It represents the energy required to move an atom of the crystal to infinity and to replace it by an impurity (iodine here) initially located at infinity.

- Finally, the incorporation energy is the energy to place a iodine atom at a pre-existing trap site [Grimes, Catlow and Stoneham 1989, Grimes and Catlow 1991].

There are two possibilities. One is to put a iodine atom at a substitutional site :

$$E_{incorporation} = E_{(Zr_{(N-1)},I)} - E_{Zr_{(N-1),vacancy}} - E_I$$

The other one is to put the iodine atom in an interstitial site :

$$E_{incorporation} = E_{(Zr_N,I)} - E_{Zr_N} - E_I$$

where $E_{(Zr_N,I)}$ is the total energy of the cell which contains N atoms of zirconium and one atom of iodine in interstitial position.

With these definitions, a negative value for the impurity or incorporation energies mean that the process is exothermic so energetically favorable.

3.2 Results with iodine in substitutional site

From a practical point of view, we have done some total energy minimization runs on cells with different configurations and with different number of atoms. We have specialized on three sizes of cells composed with 8, 18 and 36 atoms respectively. Let us note that a cell containing more that 36 atoms is too time-consuming. These cells consist of the repetition of the unit cell composed with two atoms : for example the cell with eight atoms is obtained by a multiplication by a factor of two in each direction. The three cells are presented in Figure 4. For the vacancy zirconium formation energy, we have used two different types of these cells : one composed with Natoms of zirconium and the other composed with $N-1$ atoms of zirconium and one vacancy ($N = 8, 18$ and 36). The crossed circle represents either a zirconium atom for a simulation with N atoms and a vacancy for a simulation with $N-1$ atoms. Full (empty) circles represent zirconium atoms allowed to move (fixed) during the calculation. Some atoms are not allowed to move in order to save computer time, but, of course, we checked that this does not affect the final result. Finally, for the case of incorporation and impurity energies of iodine in substitutional site, we used an other type of cell : one with $N-1$ atoms of zirconium and one iodine atom (the crossed circle in that case).

In practice, it is impossible to work with a big cell and a great number of k-points. Therefore, we have adopted the following strategy to estimate the errors produced by "simplified" calculations : firstly, we estimate the influence of the number of k-points (see Table 5) on the smallest cell and say that the resulting error would be approximately of the same order for an other cell, whatever its size (this statement has been partially checked for different cells). Then, we estimate the influence of the size of the cell for a given k-points mesh (Table 6) and say that the error would be of same order whatever the k-points mesh is. These errors are important because in one hand, we have to work with a big cell to isolate the impurity or the vacancy

and in the other hand, it is impossible to deal with a large number of k-points when working with a big cell.

Of course, we have by the way described above, a crude estimate of the error produced by the use of a small number of k-points and/or a small cell. We will see in the following that this crude estimate is actually sufficient.

The results presented in Tables 5 show that the increase of the number of k-points induced an error of 1.5% for the energy of vacancy zirconium formation, 7% for the impurity energy and 4% for the incorporation energy. In table 6, we see that the induced error is all cases less 10%.

If we combine all the numbers, we can say that the results obtained show clearly that the impurity energy is, in all cases, positive and the incorporation energy negative.

3.3 Results with iodine in interstitial site

The closed hexagonal structure of zirconium presents several interstitial sites. Considering the size of a iodine atom, we have considered the largest ones : the octahedral and tetrahedral sites. We then have built some cells composed with nine atoms: eight atoms of zirconium and one iodine atom in interstitial site.

Results are presented in Table 7. We see that the values for the incorporation energy in octahedral and tetrahedral sites are of different signs. Taking into account errors coming from the size of the cell and from the number of k-points discussed in the preceding section, these numbers keep the same sign. Thus the process consisting in putting an iodine atom in octahedral (tetrahedral) site is energetically favorable (non favorable).

4 Conclusion

In conclusion, it has been shown that iodine and zirconium pseudopotentials generated here describe accurately experimental data.

For the energy calculations with iodine in substitutional site, we show that in the closed hexagonal structure of zirconium with one vacancy, the incorporation energy must be considered and it is negative. We can conclude that the process to replace a zirconium vacancy with an iodine atom is an energetically favorable process. In a perfect crystal, the impurity energy must be considered so the process to replace a zirconium atom with an iodine

atom is endothermic, energetically defavorable. For the energy calculations with iodine in interstitial site, the energetically favorable site is the octahedral site. Nevertheless, the value of the incorporation energy of iodine in substitutional site is most negative than in octahedral site. We can conclude that the energetically favorable site is a substitutional site. Iodine diffusion in zirconium seems to be a substitutional process. This result is in agreement with an experimental study (Carlot 2000) given diffusion coefficient of iodine in zirconium and concluded to a substitutional process. An other approach from Hood (Hood 1988), combined with this experimental study, goes in that direction as well.

Although we believe the main conclusions of this work would remain unchanged, we can mention that some other effects have to be taken into account. For example, multiple diffusion process, that is a diffusion process that involve more that two atoms (three atoms, two atoms and a vacancy, etc...). Moreover, it could be interesting to compute explicitly the migration energy (part of the activation energy). This work is in progress.

Acknowledgments : We thank Henry Jaffrezic and Thierry Petit for useful discussions.

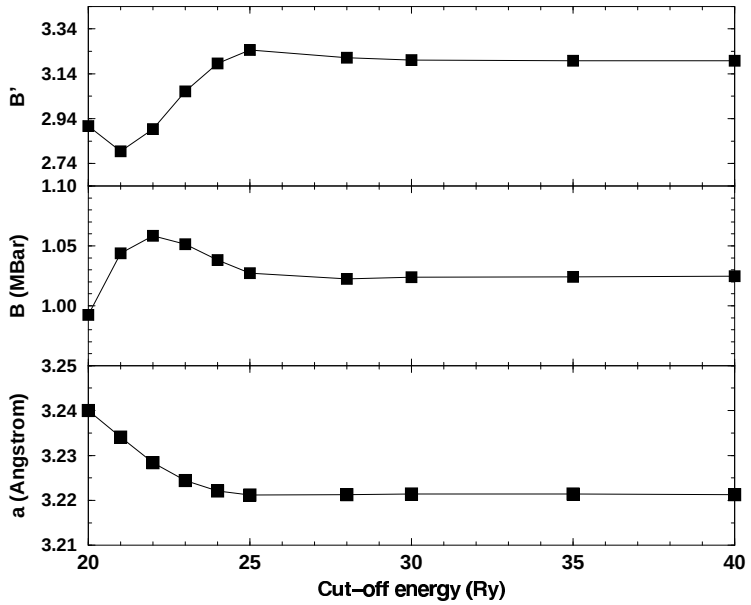

Figure 1: Constant lattice a($\mathring{A}$), bulk modulus B_0 (MBar) and the first derivated of the bulk modulus B_0' versus cut-off energy E_C for a fixed of k-points mesh (18×18×9) for the α phase.

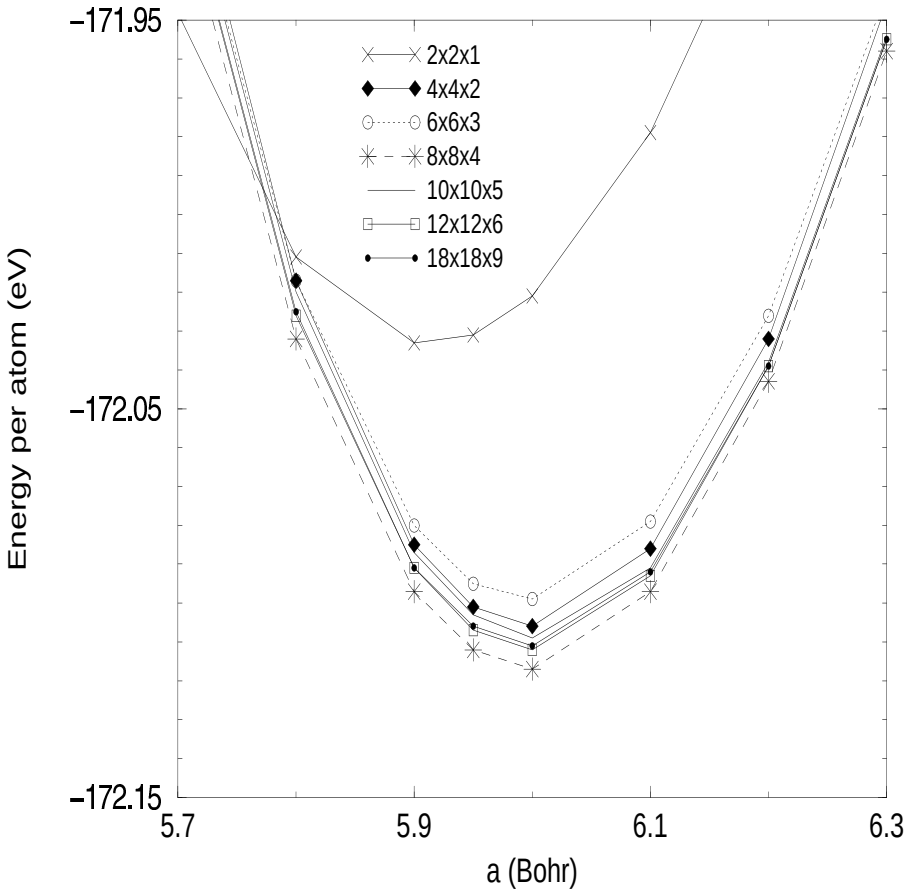

Figure 2: Calculated energy per atom (eV) of α phase versus unit cell parameter ($\mathring{A}$) for different number of k-points mesh at a cut-off energy equal to 30 Ry.

Table 1: Calculated and experimental equilibrium volume V_0 for three phases of zirconium: α, ω and β.

	$V_0(\mathring{A}^3)$ α-Zr				$V_0(\mathring{A}^3)$ ω-Zr			
	GGA	GGA 2 Bohr	LDA	LDA 2 Bohr	GGA	GGA 2 Bohr	LDA	LDA 2 Bohr
This study	23.28	23.27	20.85	21.82	23.12	22.92	20.56	21.61
Other study	23.52		22.03		23.27		21.81	
Experiment	23.273 - 23.28				22.58			

	$V_0(\mathring{A}^3)$ β-Zr			
	GGA	GGA 2 Bohr	LDA	LDA 2 Bohr
This study	23.00	22.74	20.35	21.44
Other study	22.91		21.32	
Experiment	22.28			

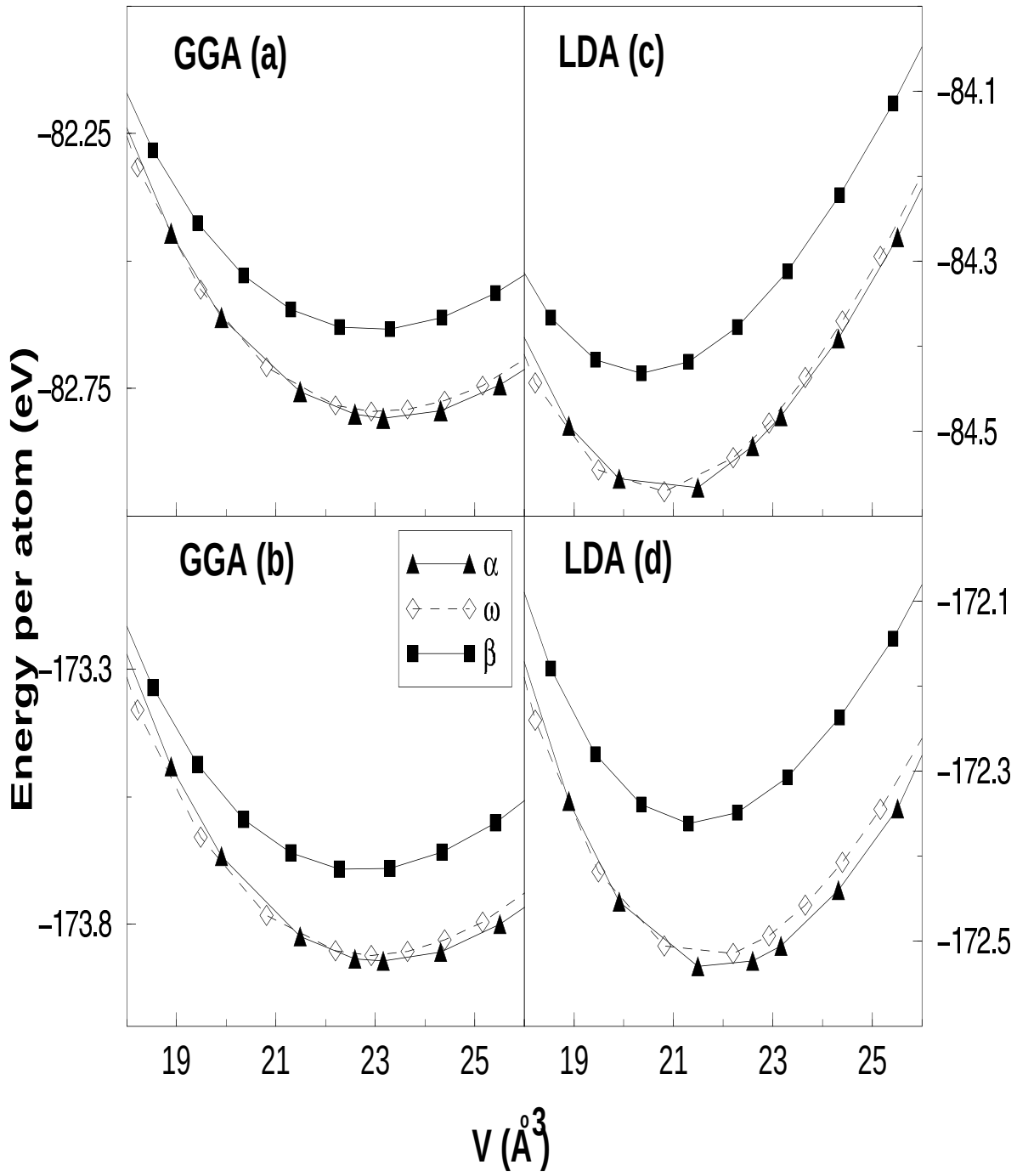

Figure 3: Calculated energy (eV) per atom versus unit cell volume ($\AA$) for zirconium a) GGA, b) GGA with a core density cut off radius equals to 2 Bohr, c) LDA et d) LDA with a core density cut off radius equals to 2 Bohr.

Table 2: Calculated and experimental data of the bulk modulus for the α phase zirconium.

	B_0(GPa)			
	GGA	GGA 2 Bohr	LDA	LDA 2 Bohr
This study	102	114	123	125
Other study	94		104	
Experiment	95			

Table 3: Calculated and experimental data for the transition pressures of the ω phase.

	$P_{\alpha\rightarrow\omega}$ (GPa)			
	GGA	GGA 2 Bohr	LDA	LDA 2 Bohr
This study	9.2	5.8	-	5.1
Other study	2.4		5.7	
Experiment	2-6			

Table 4: Calculation on the molecular iodine: vibration frequency ν, equilibrium bond distance d and dissociation energy E_d.

	ν (THz)	d ($\mathring{A}$)	E_d(eV)
This study	5.6	2.66	-1.48
Experiments	6.4	2.67	-1.54

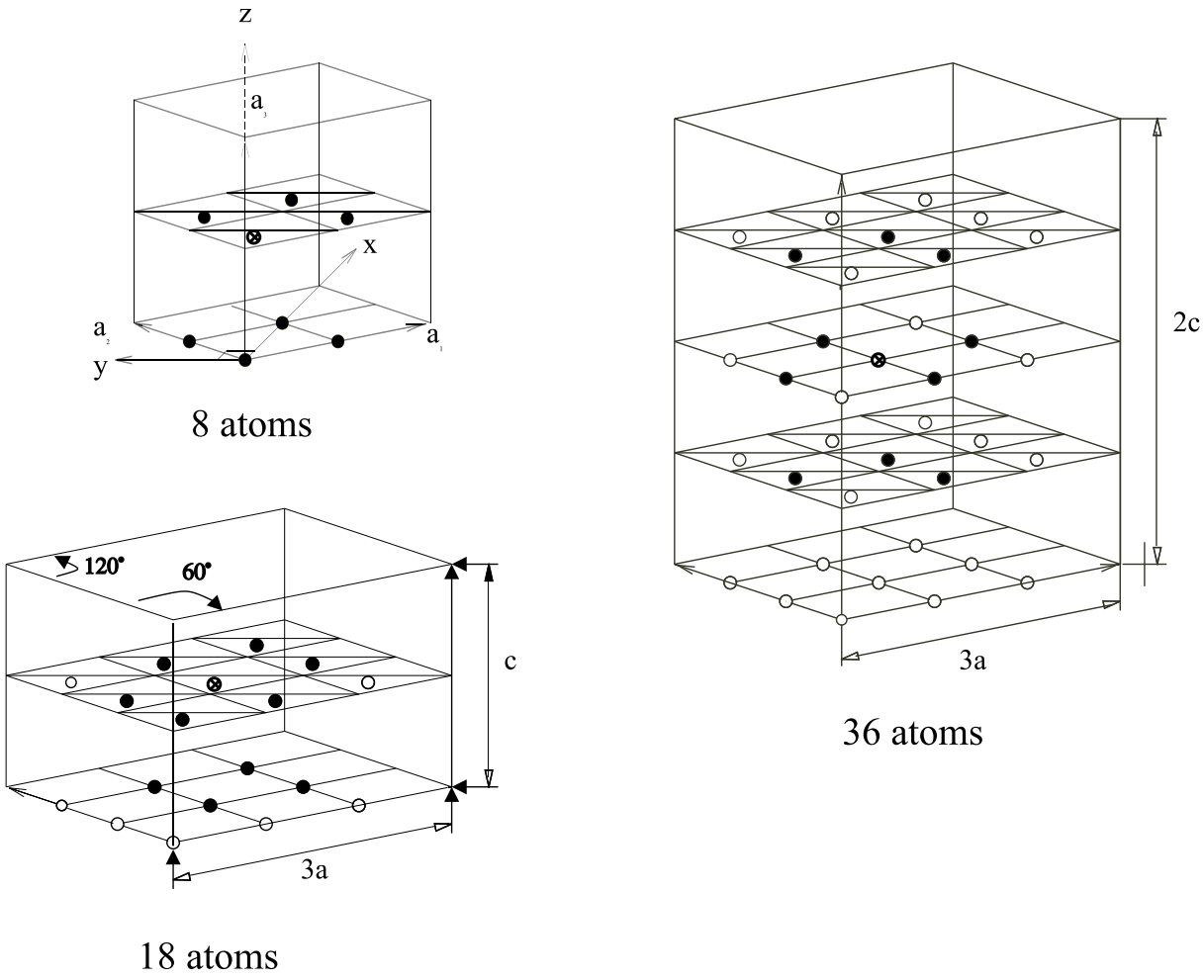

Figure 4: Cells composed with 8, 18 and 36 atoms built for computing vacancy formation energy and impurity and incorporation energies of an iodine atom in the closed hexagonal structure of zirconium. The crossed circle is whether a zirconium atom or an iodine atom or a vacancy. The full circles are zirconium atoms allowed to move and the empty circles are fixed zirconium atoms.

Table 5: Zirconium vacancy formation energy, incorporation energy and impurity energy of iodine atom substituted at a zirconium atom in a cell of eight atoms for different k-points meshes.

	Zirconium Vacancy formation energy(eV)	Incorporation energy of iodine (eV)	Impurity energy of iodine (eV)
4×4×2	1.38	-2.85	2.35
4×4×4	1.37	-2.96	2.22
8×8×4	1.36	-2.95	2.20
8×8×8	1.36	-2.95	2.21
10×10×10	1.37	-2.97	2.19

Table 6: Zirconium vacancy formation energy, incorporation energy and impurity energy of iodine atom substituted to a zirconium atom versus the number of atoms for a fixed k-points mesh (4×4×2).

	Zirconium Vacancy formation energy(eV)	Incorporation energy of iodine (eV)	Impurity energy of iodine (eV)
8 atoms	1.38	-2.85	2.35
18 atoms	1.33	-2.63	2.53
36 atoms	1.26	-2.78	2.28

Table 7: Incorporation energy of iodine in interstitial tetrahedral and octahedral site versus the number of k-points in a cell with nine atoms: eight atoms of zirconium and one atom of iodine.

	Incorporation energy of iodine in interstitial site (eV)	
	octahedral site	tetrahedral site
4×4×2	- 0.77	1.61

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